Tunneling Through a Single Quench-Condensed Cluster

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Quench-condensed bismuth films of 3-5 nm thickness have been used as a cluster source to prepare Single Electron Transistors (SET) based on a single cluster with high charging energy. We used electron-beam defined shadow evaporation masks to pattern 10 nm wide constrictions in these films. By incremental depositions through these masks controlled by in situ sample conductance measurements, we obtained a SET geometry for clusters with charging energies up to 90 meV. Our experiment showed that the SET geometry can be achieved in every sample preparation run, despite the apparent random nature of cluster formation in granular films. The resulting charging energy of the transistor varied from experiment to experiment. Its value, however, was always higher than 10 meV.

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1. SINGLE ELECTRON TRANSISTOR (SET) GEOMETRY FOR A SMALL CLUSTER

Tunneling through a particular nanometer sized grain allows one to work at the border between atomic[1] and mesoscopic[2] physics. One fundamental achievement in this field is the observation of single-electron states in a small metallic grain, allowing a detailed study of complex systems with electron-electron interaction[3]. Tunneling through a small cluster can be interesting for applications, as a high charging energy implies a high working temperature of the transistor based on this cluster.

Recently, two successful ways have been used to select one grain and to place it in a single electron transistor geometry. In one approach, tunneling contact with a particular grain was achieved in a 'vertical' geometry with a hole in a silicon nitride membrane, where the top and bottom electrodes are connected by chance via a few nanometer metallic dot[4]. In the experiments of Klein *et al.*[5], instead, a lateral geometry was used. Closely spaced electrodes, prepared in advance, were covered with a number of nanoclusters. Due to the exponential nature of tunneling, a single grain, appropriately placed between the electrodes, controlled the transport in the device.

Unfortunately, there is very little control of the sample geometry at these sizes and measurements in the experiments described above have been performed on selected samples demonstrating a proper behavior. Different techniques of self-assembly, promising a better control of the sample properties, are currently under development[6].

In the present work we study metallic clusters grown on the substrate held at helium temperature between self-aligned electrodes. Our experimental technique allows one to monitor the sample properties during the sample preparation, while the sample topology is changing by the increase of the film thickness in the constriction.

Cryovacuum conditions insure clean tunneling surfaces of the cluster. This, together with a reduced diffusion at low temperature, resulted in high sample stability between film depositions. After the initial stage of multigrain nanoconstriction structure, a single electron transistor geometry has been routinely achieved. Regular Coulomb diamonds were observed in the best samples, in contrast to the reported properties of other lateraly confined nanostructures with irregular (though reproducible) gate dependence[7]. Further depositions lead to a single tunneling gap geometry. Finally, at higher film coverage, a metallic nanocontact has been formed.

2. QUENCH - CONDENSED FILMS AS A SOURCE OF CLUSTERS

The technique of quenching the metal vapor on a cold substrate was pioneered by Shal'nikov[8]. The low mobility of metallic atoms on a cold substrate leads to a high degree of disorder in these films. Metallic quench-condensed films grown on insulating substrates exhibit transformation from insulating to conducting state as the film thickness increases. For most metals this transition happens at very low average film thickness d_{C}. A common belief is that at film thickness $d < d_{\mathrm{C}}$ a metal on an inert substrate forms islands separated by tunneling gaps. The high charging energy of small islands leads to insulating properties of the whole film. As the film thickness is increased, these islands merge, and, finally, a percolating metallic path through the whole film appears at $d = d_{\mathrm{C}}$. The mechanism of island formation on the low temperature substrate with low atomic mobility is poorly understood. However in recent STM experiments by Ekinci and Valles[9] their existence is confirmed experimentally for Pb (d_C = 5 nm) and Au (d_C = 2.5 nm). An unusual growth scenario has been found. The island formation occurs suddenly by an avalanche in the amorphous precursor layer. Clusters with charging energies as high as 0.2 eV are reported in these experiments. Although the formation process of quench-condensed films is unknown, they seem to be an attractive source of small metallic clusters.

In the present work we have used bismuth films. The critical thickness in a wide film is 1-2 nm. In a constriction, where many conduction paths are frustrated, it may be higher. Bi QC films are known to be amorphous[11], and the scenario presented in Ref. 9 is not directly applicable. However, there are no doubts about the existence of the granular structure of thin Bi films prepared on neutral substrates (see, for example, Haviland and Goldman[10]). Our experiments confirm this statement.

Our studies of granular thin films in nanoconstrictions can be considered as complementary to the STM study by Ekinci and Valles. We perform local transport measurements through a single cluster, isolated from the rest of the structure by tunneling barriers, which naturally appeared during the film growth. The high electric fields, which can be applied to the cluster, are impossible in a bulk transport geometry.

3. NANOFABRICATION

The idea of nanofabrication has been described in Ref. 12 and resulted in a room temperature operating SET. We will shortly report the main points of the procedure. The main obstacle to using electron-beam masks down to 10 nm feature size is their poor reproducibility at this level, at least, under ordinary laboratory conditions. We overcame this drawback by tuning the effective size of the mask during the process of sample fabrication. Angle evaporation was used to reduce the effective width of the constriction; *in situ* sample conductance measurements helped to find the proper angle when the constriction is just open (see Fig. 1). All further deposititions to form the transistor occured at this angle.

The effective width of the mask for the first conductive sample did not exceed the nominal value of step in the opening of the constriction, which was 10 nm. The minimum step size was limited by the danger of closing the mask by the deposited material. To reduce this effect we used a metal with low d_C (after each step in tilt angle, widening the gap, we deposited a test metallic layer with a thickness $2 \times d_C$ and checked the sample conductivity

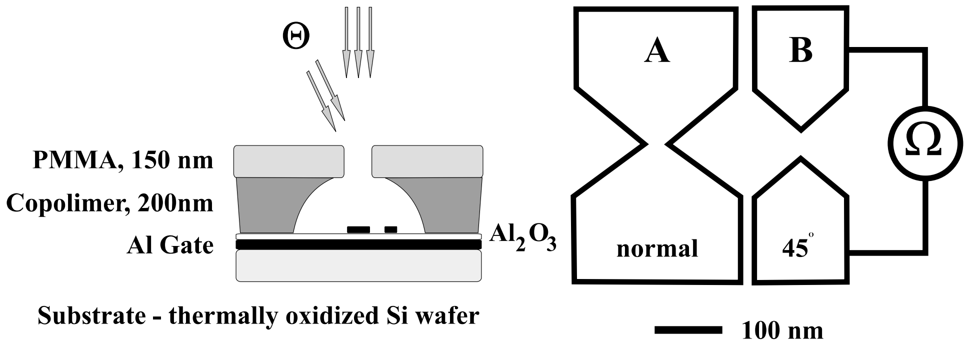

Fig. 1. Left - reduction of the effective size of the opening in the resist by angle evaporation. Right - tuning the constriction size: starting from $\Theta = 45^o$, where the constriction is closed (contour **B**), the tilt Θ was decreased stepwise with a step of about 5^o, to open it by 10 nm in every step. After each tilt decrement about 2 nm of material were deposited to check if the connection appeared. Contour **A** is a sketch of the mask shape without its reduction by angle evaporation.

to determinine if the effective constriction in the mask was opened). In a number of experiments we have successfully tried a step size of 5 nm.

4. CRYOSTAT WITH FILM DEPOSITION CHAMBER

In the cryostat we have combined high vacuum facilities and the possibility to keep our sample at various temperatures from 2 K to 300 K. Our vacuum system uses cryopumping on the walls of the vacuum chamber, which is completely immersed in liquid helium. This is a standard way of producing a vacuum environment approaching UHV, since the vapor pressure of all the gases is negligible at liquid helium temperature 4.2 K. In such clean conditions we were able to prepare extremely thin metallic films (1-3) nm with very small incremental steps, without the danger of sample contamination in the time between evaporation steps.

A mechanical feedthrough, controlled by a stepping motor placed at room temperature, allowed precise tilting of the substrate inside the vacuum chamber. A mechanical shutter was used to stop film deposition. A quartz crystal film thickness monitor was placed next to the substrate. All the figures for the average film thickness were obtained assuming the density of bulk bismuth.

The usual procedure consisted of pumping out the chamber with a turbomolecular pump, and cooling the chamber down to liquid nitrogen temperature. A computer controlled heater kept the substrate holder at about 40^o C, preventing contamination of our substrate during this procedure. Then, keeping the substrate warm and still pumping the chamber, we filled our dewar with liquid helium. When the tube connecting the chamber with the turbomolecular pump became cold, we could separate the turbo pump from our system with a valve and turn the pump off. After this procedure vacuum conditions did not change as long as we kept liquid helium in the cryostat.

We believe that cryopumping on the surfaces at helium temperatures produced residual pressures lower then 10^{-10} Torr in the vacuum chamber. In fact, we did not observe any effect of aging in our samples, which could be attributed to poor vacuum conditions: samples did not change their properties for several days.

We were able to evaporate bismuth using a small, well-shielded, resistively heated evaporator. The capacity of our evaporator corresponds to 1000 Å of a film thickness on the substrate. The power dissipated in this evaporator is about 2 W. The film deposition warmed the substrate up to 5 K, as we observed using a Silicon diode thermometer attached to the sample.

5. GROWING THE TRANSISTOR

The first conductive sample has a simple geometry: relatively thick (6-8 nm) closely spaced low resistive electrodes, formed in the process of finding a proper tilt angle (see Fig. 1), were bridged by a narrow network of metallic clusters. In the constriction of 10 by 10 nm one can imagine a maximum of 4 by 4 clusters with the typical size of 2 nm.

We studied the evolution of the sample electrical properties as a function of film thickness in the constriction. After each small increment of film thickness we took extensive measurements of the current-voltage characteristics at different gate voltages. Thus, in one experimental run, more than 30 different samples were prepared and characterized. A generalized picture derived after a number of experimental runs is presented in Fig. 2. It shows the sample resistance (nominal value) as a function of the film thickness in the constriction, taken during one experimental run (Fig. 2a).

Three regions with very different behavior can be clearly seen. We shall discuss them starting from the lowest film thickness.

The region with fluctuating resistance corresponds to modification of the grain sizes and changing of the tunneling gaps between them under the influence of incoming atoms. All the samples from this region demonstrated

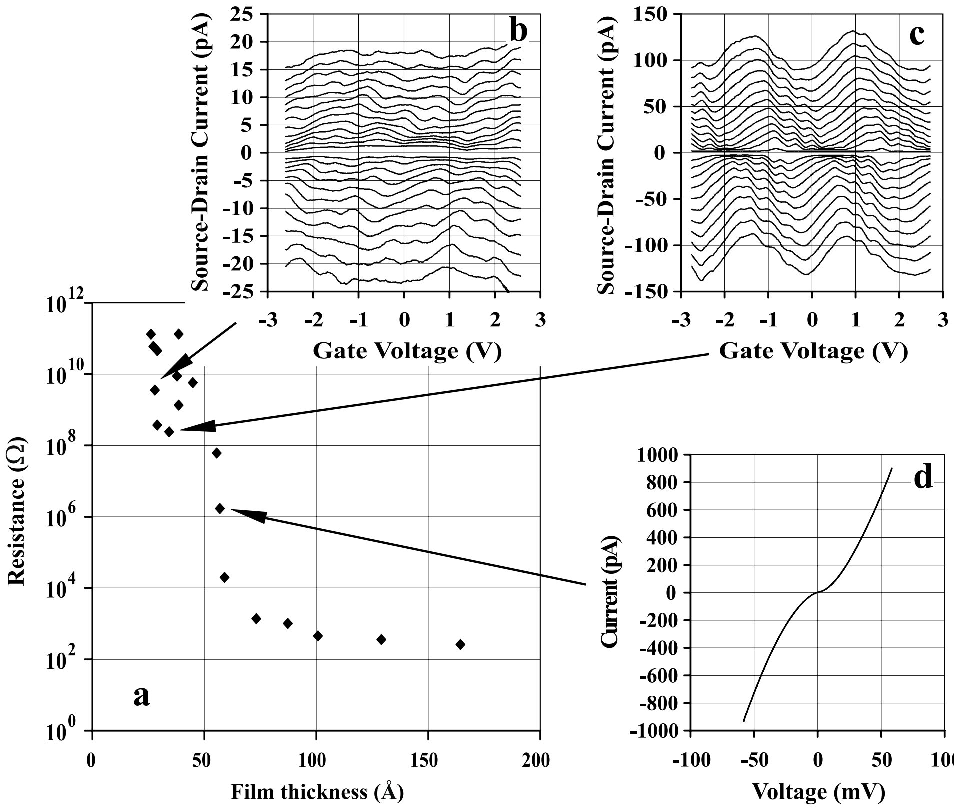

Fig. 2. **a** - The nominal value of the constriction resistance as a function of the film thickness. Electrical properties of selected samples indicated by arrows are demonstrated in more detail: **b**,**c** - Gate dependence of the tunneling current through the constriction. Bias voltages are equidistantly spaced in the region ±600 mV; **d** - Current-voltage characteristic of a single tunneling barrier in the constriction. It does not change with the gate voltage. T = 4.2 K.

sensitivity to the electrostatic gate, as it is shown in Fig. 2b,c.

Despite the apparently random change of the resistance from sample to sample, due to the strong distance dependence of the tunneling resistance, in each experiment we observed a steady increase in the regularity of the Coulomb blockade oscillations with increasing film thickness in the constriction. This evolution brings us to samples with almost perfect Coulomb diamonds and regular gate dependence. They correspond to the geometry of Single Electron Transistor, with a single grain separated by tunneling barriers from two metallic electrodes. From the experiments with coupled

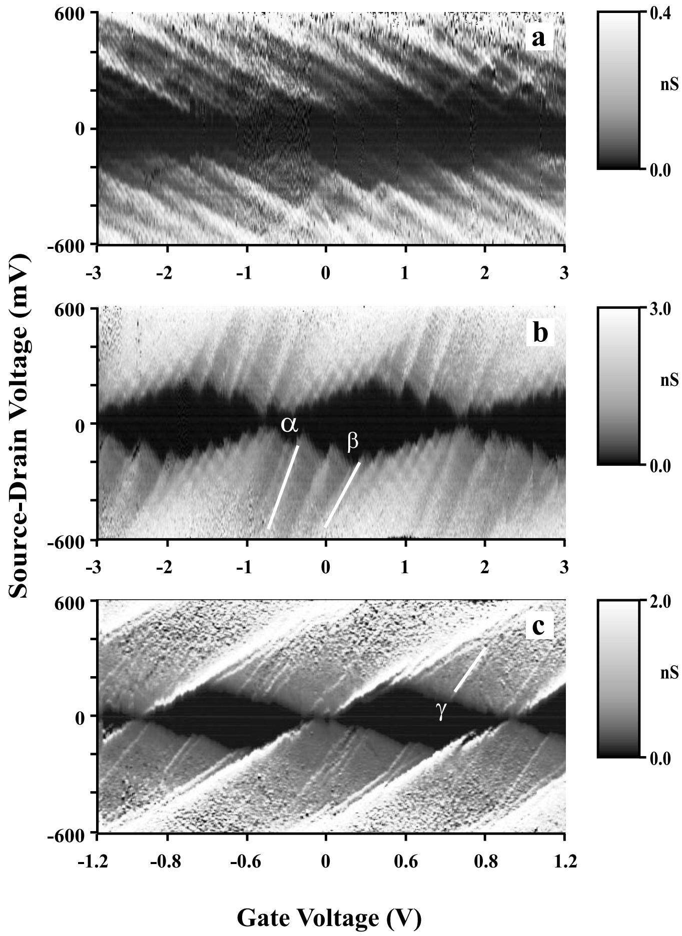

Fig. 3. Gray scale derivative plot for some samples from Fig 2. **a** - the same sample as in Fig. 2b, tunneling through many clusters; **b** - the same sample as in Fig. 2c, 2 islands in a chain. Note a different slope for α and β lines due to mutual interference; **c** - Next deposition step after the sample **b**: one island left, see discussion in the text. T = 4.2 K.

quantum dots[13] we know how sensitive the shape of diamonds is to the presence of a second grain connected in series. Therefore, we attribute the increase of sample quality to the diminishing of the number of clusters influencing the current. Disrupted Coulomb diamonds at low film thickness finally evolve to a regular gate modulation corresponding to just one cluster left[14]. In Fig. 3 it is demonstrated how we could determine the presence of a single island controlling the tunneling through the constriction.

At a certain step the deposited metal attaches the central island to one of the leads, leaving just one tunneling gap in the constriction (Fig. 2d). The gate dependence is no longer observed. The sample resistance drops exponentially as the remaining gap is closing by further depositions.

When the amount of metal in the gap increased even further, the last tunneling barrier evolves to a metallic nanocontact with a resistance of a few kΩ. One can see in Fig. 2a the transition from an exponential to a power law dependence of the contact resistance with the film thickness.

6. DISCUSSION

The tunneling spectroscopy measurement of small clusters is a challenging goal. It requires a perfect SET transistor geometry. It was not obvious that such a clean geometry could be achieved by a rather simple technique involving random growth of granular film. Our experiment shows that it is possible.

Fig. 3c shows spectroscopic data for the transistor built around a single cluster with two well-developed Coulomb diamonds and pronounced Coulomb steps. Some additional structures are also present. One can see a set of bright lines, reflecting enhanced differential conductance of the sample. At low biases these lines tend to align parallel to each other, though their common angle γ is different from the angles formed by the main Coulomb diamonds. As the bias is increased, these lines stick to the Coulomb steps. They are quasiperiodic with the main period of the transistor and tend to aggregate into clusters within one period.

The nature of these peculiarities is not known at present, but we believe that they are not artifacts of other grains in the constriction[15] and reflect some intrinsic properties of the main grain in the transistor.

Indeed, two separate transistors, connected in series, can be easily modelled numerically. The resulting behavior looks like Fig. 3b, where the mutual influence of the two transistors, sharing common bias voltage, causes a variation of the slopes α and β.

The position of all peculiarities on $\mathrm{d}I/\mathrm{d}V(V_{\mathrm{Bias}}, V_{\mathrm{Gate}})$ grayscale plot can be found analytically for a system of two coupled grains. The result of calculations shows that within the regions of a constant charge on the first grain (constricted by the main staircases in Fig. 3c) all peculiarities coming from the second grain are *straight* lines (in contrast to Fig. 3c, where they are curved when approaching the staircase), *parallel* to each other (this is the case), and exactly *equidistant* (in Fig. 3c they are obviously aggregated into clusters). Thus all attempts to explain the spectroscopic data from Fig. 3c by the presence of additional grains fail.

From Fig. 3c we can find the parameters of the main transistor[16]. Its charging energy is 93 meV and the estimated cluster radius is approximately 1.3 nm. Such a small cluster would contain about 400 bismuth atoms and 2000 valence electrons. Is it possible to observe individual electron levels in this cluster or they will be smeared for some reason? For certain, we do not see a classical picture of levels, typical for metallic or semiconducting quantum dot spectroscopy (see Ref. 4,13 for example), but we can not exclude the electronic shell structure[1] as the origin of the observed anomalies.

In such a small cluster some mechanisms, different from those considered in Ref. 17, could be responsible for the level smearing, such as nonequilibrium effects due to the tunneling current. The electrostatic effects from charging this cluster by one electron may affect its equilibrium shape and, as a consequence, its spectrum. This effect would contribute to the level smearing too and, in turn, give rise to its own peculiarities in dI/dV. According to our simulations, electromechanical reconstruction of the cluster, occuring at a certain electric field, may also lead to structures similar to those observed in Fig. 3c.

7. CONCLUSIONS

We have demonstrated a fabrication technique which permits tunneling through a particular cluster with charging energies of the order of tens of millielectronvolts. Most of the cluster surface remains free during both sample preparation and measurement. This circumstance makes our samples different from these prepared by other techniques, where the cluster shape is stabilized, for example, by chemical interaction with the oxide layer, which forms the tunneling barrier. In this sense our spectroscopic measurements are closer to STM spectroscopy in metallic nanoclusters, but we have a much higher stability of the electrodes and electrostatic gate.

To our knowledge, transistors with such a high charging energies have not been reported before. We believe that deviations from the common picture reported in this paper are due to the extremely small cluster size, realized in our experiment, and its free surface.

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14. Typically, when the main transport chain is reduced to a single cluster, we can see some perturbation of the diamond structure coming from a long-range capacitance coupling to nearest islands. Their presence reveals in periodic lines crossing the gray scale plot of derivatives. In most cases, further depositions improved the transistor quality by merging these islands either with the leads or with the main island.
15. A system with more than 2 grains will always demonstrate a staircase pattern with more then 3 different slopes. As we see only 3 slopes in Fig. 3c (2 from the Coulomb diamonds plus one additional slope γ), we conclude that there can be no more than 2 grains in this system.
16. A fit to orthodox model for this transistor gives the following parameters: $C_1 = 2.3 \times 10^{-19}$ F; $C_2 = 4.6 \times 10^{-19}$ F; $C_{\mathrm{G}} = 1.7 \times 10^{-19}$ F; $R_1 + R_2 = 2,3$ GΩ; $E_{\mathrm{C}} = e/2C_\Sigma = 93$ meV.
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